J|A|C|S
COMMUNICATIONS

Synthesis of Silica Hollow Nanoparticles Templated by Polymeric Micelle with Core−Shell−Corona Structure

Anil Khanal, Yuko Inoue, Mitsunori Yada, and Kenichi Nakashima*

Department of Chemistry, Faculty of Science and Engineering, Saga University,
1 Honjo-machi, Saga 840-8502, Japan

Received December 6, 2006; E-mail: nakashik@cc.edu-saga.ac.jp

Recently, the synthesis of inorganic hollow nanoparticles has attracted much attention in the chemistry and material communities because of their low density, large specific area, mechanical and thermal stabilities, and surface permeability.[1] Such hollow nanoparticles have a wide variety of potential applications in cosmetics, catalysis, coatings, composite materials, dyes, ink, artificial cells, and fillers. Furthermore, their hollow structure can be used as a microencapsulate for drugs in the pharmaceutical fields.[2]

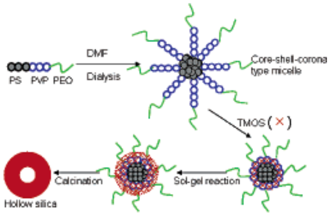
Thus, various methods, such as templating, sonochemical, and hydrothermal methods, have been reported as the procedures for the preparation of inorganic materials with hollow spherical structures. In recent years, the use of sacrificial templates to fabricate such hollow spherical nanoparticles has proven successful.[3−6] Especially, there has been growing use of polymer nanoparticles such as latexes and polymeric micelles because it is easy to control the size, morphology, and surface functionality of the polymer nanoparticles. Generally, latex particles are employed for fabricating hollow particles with relatively larger diameters ranging from submicrometers to micrometers, while polymeric micelles are used for smaller hollow particles with diameters of less than one hundred nanometers.[7]

Although there have been many studies of latex templates,[8] a few reported the use of templates of polymeric micelles. One of the advantages of templates of polymeric micelles is that the size and morphology of the micelles can be easily tuned by adjusting the block size, polymer combination, and solvent composition. The polymeric micelles so far employed have a *core−corona* type architecture formed from AB diblock or ABA triblock copolymers.[9−12] In these systems, the corona of the micelles acts as a reservoir of the precursor of the inorganic material, and the core acts as a template of the hollow. The precursor of the inorganic material is sorbed (or adsorbed) into the corona of the micelles, and forms the shell of the hollow particle after being polymerized. The core-forming polymer is removed by calcination or other appropriate techniques that leaves a void volume inside the inorganic shell. In this method, however, the template micelles become very unstable when the precursor is sorbed into the corona, leading to the formation of second-order or higher-order aggregates in which two or more particles are bound to each other.

To avoid the problem associated with the AB diblock and ABA triblock copolymer micelles, we tried to use ABC triblock copolymer micelles with a *core*−shell−corona structure as a template. In our system, the precursor of the inorganic material is designed to be selectively sorbed into the shell in order that the corona is free from the precursor that keeps the micelles stable.

As the first example of our method, we now report the synthesis of hollow silica particles templated by the micelles of poly (styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) (PS−PVP−PEO). Although silica hollow spheres have been reported by many groups, most of them possess nonuniform shapes, have a shell of an undesirable thickness, lack structure stability, and require high-temperature routes.[13]

Scheme 1. Fabrication of Hollow Silica Nanosphere from PS−PVP−PEO Micelle Template



The micelles of the PS−PVP−PEO triblock copolymer has been well characterized by Gohy et al.,[14−16] Stepanek et al.,[17] and our group.[18−21] It has been shown that the micelle has a glassy and hydrophobic PS core, an ionizable hydrophilic PVP shell, and a hydrophilic PEO corona. The PVP shell extends at low pH (<5) owing to repulsive forces among the protonated PVP units.[16] The addition of the anionic species into this micelle cancels the positive charge of the PVP unit, resulting in a morphological change in the PVP shell from an extended to a shrunken form.[18−21] These behaviors of the PS−PVP−PEO micelle seem to be utilized to selectively deposit the silica on the PVP block of the micelles by the following two reasons: (i) the protonated PVP block is known to act as an acid catalyst site for the hydrolysis of tetramethoxysilane (TMOS), a precursor of silica,[22,23] and (ii) silica has a negative charge at pH 4 in order to strongly bind to the protonated PVP block.[24] Scheme 1 shows a procedure for fabricating hollow silica nanospheres by the sol−gel technique combined with a template of the PS−PVP−PEO micelle.

It should be noted that PEO is known to form crown-ether-type complexes with the silanol groups of silica through hydrogen bonding.[25] Thus, there is a possibility that the silica precursor is also bound to the PEO corona of the template micelles. However, such an interaction is prominent at pH 1, but weak at pH values ranging from 2 to 7.[25] Therefore, we believe that silica networks are mostly grown on the PVP block of the micelle in comparison to the PEO block.

PS−PVP−PEO was obtained from Polymer Source, Inc. The molecular weight of each block is M_n (PS) $= 14100$, M_n (PVP) $=$ 12300, and M_n (PEO) $= 35000$.

The micelle of PS−PVP−PEO was prepared according to the method of Gohy et al.[14,16] First, 0.1 g of PS−PVP−PEO was dissolved in a mixture of 0.5 g water and 4.4 g *N*,*N*-dimethylformamide (DMF). The solution was stirred for several days until the PS−PVP−PEO polymer was completely dissolved. The solution was then dialyzed against water to obtain the micelles of PS−PVP−PEO. The pH of the solution was adjusted to 4 with a diluted HCl solution (step 1 in Scheme 1). The PS−PVP−PEO micellar solution

10.1021/ja0684904 CCC: $37.00

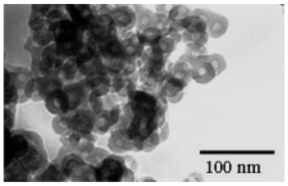


Figure 1. TEM picture of hollow silica nanosphere prepared by templating the PS−PVP−PEO micelle. The concentration of the PS−PVP−PEO is 0.9 g/L and the molar ratio of PVP/TMOS is 1:23.

was slowly stirred for 2 days after the desired amount of TMOS was added. The solution was then stored for 4 days without stirring to allow the silica network to be formed by the sol−gel reaction (steps 2 and 3 in Scheme 1). After the sol−gel reaction was completed, the solution was dried at 50 °C for several hours to obtain a powder of the silica/PS−PVP−PEO composites. The composites were heated at the rate of 1 °C $\min^{-1}$ and calcined in a furnace at 500 °C for 4 h in air to remove the template polymer (step 4 in Scheme 1).

Figure 1 illustrates the transmission electron microscope (TEM) image of hollow silica spheres obtained after calcination of the composites of the silica and PS−PVP−PEO which was prepared at a molar ratio of PVP to TMOS of 1:23. Almost all the hollow silica has a spherical shape with smooth shell. The average outer diameter of the silica particle is 30 nm, and the average diameter of the hollow (void space) is 11 nm. The wall thickness of the shell is 10 nm.

Gohy et al. measured the diameter of the PS core and thickness of the PVP shell for the neat micelle of PS−PVP−PEO with the same block lengths as ours.[16] According to them, the diameter of the PS core is 14 nm irrespective of the pH, while the shell thickness of the PVP block is 5.5 nm at $\text{pH} > 5$ and 8.5 nm at $\text{pH} < 5$.[16] Their data well support our idea shown in Scheme 1. It is obvious from Scheme 1 that the PS core of the PS−PVP−PEO micelle directs the void space of the hollow silica. If we compare the diameter of the void space of the hollow silica (11 nm) with that of the core of the template micelle (14 nm), we realize that their values are close to each other. The slight difference between the two diameters implies that the hollow silica particles were shrunk during calcination. This type of shrinkage of the hollow spheres was observed by us[26] as well as by another group[27] during the fabrication of hollow titania particles.

We examined the effect of the precursor concentration on the structure of the hollow particles. We changed the molar ratio of PVP/TMOS from 1:5 to 1:35 while keeping the concentration of the PS−PVP−PEO constant (0.9 g/L). When the molar ratio of PVP/TMOS was 1:5, we could not obtain a hollow silica nanosphere. The hollow silica was obtained if the PVP/TMOS molar ratio was increased to 1:10 (Supporting Information, Figure S1). However, the size of the void space and the thickness of the silica shell are not very homogeneous as in the case of 1:23 (Figure 1). The average values of the outer diameter, thickness of the shell, and void diameter of the hollow silica particles are 20, 6, and 11 nm, respectively. We further increased the PVP/TMOS molar ratio to 1:35. In this case, we obtained heavily aggregated hollow particles as shown in the TEM images (Figure S2). The border of each hollow particle is not distinct. The excess amount of the precursor seems to bind several hollow spheres to form the merged particles. It should be noted, however, that the diameter of the void space of the hollow particles is almost constant (average value: 11 nm). Therefore, the size of the void volume of the hollow particles seems to be precisely controlled by the size of the PS core when the concentration of the TMOS precursor is high enough to construct a strong shell wall.

In summary, we have successfully prepared a hollow silica nanosphere with a high uniformity in size using a template of the ABC triblock copolymer micelle with a core−shell−corona architecture. This route is simple when compared to other techniques like the layer-by-layer method, and the shell thickness can be controlled by changing the concentration of the inorganic precursors. It is also suggested that the void volume of the hollow particle can be controlled by the size of the PS core (that is, the chain length of the PS block). The most prominent feature of this approach is that a hollow inorganic nanosphere can be prepared by selectively depositing the inorganic material in the targeted microcompartment of the ABC triblock copolymer micelle.

Acknowledgment. A. K. acknowledges the postdoctoral fellowship for foreign researchers from the Japan Society for the Promotion of Science (JSPS). The present study was supported by a Grant-in-Aid for Scientific Research (No. 17510088) from JSPS.

Supporting Information Available: Additional TEM images of hollow silica nanospheres. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Caruso, F. *Adv. Mater.* **2001**, *13*, 11−22.
(2) Ameller, T.; Marsaud, V.; Legrand, P.; Gref, R.; Renoir, J.-M. *Int. J. Cancer* **2003**, *106*, 446−454.
(3) Kim, S. W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642−7643.
(4) Bourlinos, A. B.; Karakassides, M. A.; Petridis, D. *Chem. Commun.* **2001**, *16*, 1518−1519.
(5) Schmidt, H. T.; Ostafin, A. E. *Adv. Mater.* **2002**, *14*, 532−535.
(6) Fowler, C. E.; Khushalani, D.; Mann, S. *J. Mater. Chem.* **2001**, *11*, 1968−1971.
(7) Bergbreiter, D. E. *Angew. Chem., Int. Ed.* **1999**, *38*, 2870−2872.
(8) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111−1114.
(9) Kramer, E.; Forster, S.; Goltner, C.; Antonietti, M. *Langmuir* **1998**, *14*, 2027−2031.
(10) Qi, L.; Li, J.; Ma, J. *Adv. Mater.* **2002**, *14*, 300−303.
(11) Zhang, D.; Qi, L.; Ma, J.; Cheng, H. *Adv. Mater.* **2002**, *14*, 1499−1502.
(12) Ma, Y.; Qi, L.; Ma, J.; Cheng, H. *Langmuir* **2003**, *19*, 4040−4042.
(13) Sun, Q.; Kooyman, P. J.; Grossmann, J. G.; Bomans, P. H. H.; Frederik, P. M.; Magusin, P. C. M. M.; Beelen, T. P. M.; Van Santen, R. A.; Sommerdijk, N. A. J. M. *Adv. Mater.* **2003**, *15*, 1097−1100.
(14) Gohy, J. F.; Willet, N.; Varshney, S.; Zhang, J. X.; Jérôme, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 3214−3216.
(15) Lei, L.; Gohy, J. F.; Willet, N.; Zhang, J. X.; Varshney, S.; Jerome, R. *Macromolecules* **2004**, *37*, 1089−1094.
(16) Gohy, J. F.; Willet, N.; Varshney, S.; Zhang, J. X.; Jérôme, R. *e-Polym.* **2002**, No. 035.
(17) Stepanek, M.; Humpolickova, J.; Prochazka, K.; Hof, M.; Tuzar, Z.; Spirkova, M.; Wolff, T. *Collect. Czech. Chem. Commun.* **2003**, *68*, 2120−2138.
(18) Khanal, A.; Li, Y.; Takisawa, N.; Kawasaki, N.; Oishi, Y.; Nakashima, K. *Langmuir* **2004**, *20*, 4809−4812.
(19) Li, Y.; Khanal, A.; Kawasaki, N.; Oishi, Y.; Nakashima, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 529−533.
(20) Khanal, A.; Nakashima, K.; Kawasaki, N.; Oishi, Y.; Uehara, M.; Nakamura, H.; Tajima, Y. *Colloid. Polym. Sci.* **2005**, *283*, 1226−1232.
(21) Khanal, A.; Nakashima, K. *J. Controlled Release* **2005**, *108*, 150−160.
(22) Cho, G.; Jang, J.; Jung, S.; Moon, I.-S.; Lee, J.-S.; Cho, Y.-S.; Fung, B. M.; Yuan, W.-L.; O'Rear, E. A. *Langmuir* **2002**, *18*, 3430−3433.
(23) Fujita, N.; Otsuka, H.; Takahara, A.; Shinkai, S. *Chem. Lett.* **2003**, *32*, 352−353.
(24) Trotter, H.; Zaman, A. A.; Partch, R. *J. Colloid Interface Sci.* **2005**, *286*, 233−238.
(25) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548−552.
(26) Syoufian, A.; Inoue, Y.; Yada, M.; Nakashima, K. *Mater. Lett.,* in press **2006**.
(27) Li, G. K.; Zhang, Z. C. *Mater. Lett.* **2004**, *58*, 2768−2771.

JA0684904